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EXTRACTIVE SEPARATION OF LA AND ND USING IONIC LIQUID AS EXTRACTANT

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Abstract

Significant amounts of Rare Earth Metals (REMs) are being used for various purposes because of their unique features. Therefore, it is necessary to develop a process which can extract and separate the individual REMs efficiently. The present investigation deals with the solvent extraction and separation of light rare earth elements such as La and Nd from the chloride medium using an ionic liquid (IL) such as [$R_3N^+.Cy272^-$] as an extractant. Various parameters were investigated to optimize the conditions for separating La(III) and Nd(III) of 10^{-4} M concentration each. At pH 4.0, 90% Nd(III) and 20% La(III) were extracted from the chloride solution. The $pH_{0.5}$ values for La(III) and Nd(III) were found to be 4.5 and 3.7 respectively. Extraction of La(III) and Nd(III) increased with the increase in IL concentration. At pH 4.5 and IL concentration of 0.01M separation factor ($\beta_{Nd/La}$) of Nd(III) over La(III) was found to be 49. This shows that synthesized ionic liquid has sufficient potential to separate lighter lanthanides (e.g. La and Nd) from their mixed solutions generated during the processing of the REMs from primary or secondary resources.

Keywords: Solvent extraction, Rare Earth Metals, Ionic Liquid, Separation factor

1. Introduction

Rare earth metals (REMs) are widely utilized in automobile catalytic converters, phosphors in color television and fluorescent tubes, fluid cracking catalyst, permanent magnets and rechargeable batteries for electric and hybrid vehicles [Rare Earth Elements: The Global Supply Chain 2012]. Rare earth elements (REEs) particularly La and Nd are present in significant amounts in some primary/secondary resources viz. monazite, Ni-MH batteries, spent catalyst etc. Because of similar physical and chemical behavior of the lanthanides, their extraction and separation are the biggest challenge. Solvent extraction is one of the most promising hydrometallurgical techniques which are widely used for the extraction of several metals including that of rare earth elements [Banda et al., 2012].

Morais and Ciminelli [2004] developed a solvent extraction procedure for the recovery of 99.9% pure La_2O_3 from a chloride solution of light REEs (La, Pr, Nd) using di-2-ethyl hexyl phosphoric acid (DEHPA) and 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester [HEH(EHP)] as the extractants. A process has been developed for the recovery of Nd_2O_3 from the solution of light rare earths using PC 88A [Thakur et al., 1993]. A complexing agent (lactic acid) along with di-(2-ethylhexyl) phosphoric acid (P204) has been tried to achieve better selectivity for separating LREEs [Yin et al. 2013]. Banda et al.[2012] discussed the separation of La from Pr and Nd by solvent extractant process using various extractants- D2EHPA, PC 88A, Cyanex 272 and Cyanex 301. Cyanex 272 has shown the best extraction performance for Pr(III) and Nd(III) in comparison to La(III). While using the saponified Cyanex272, some beneficial effect relating to the pH control on the extractive separation of La(III) from Pr(III) and Nd(III) was noticed.

Recently ionic liquid (IL) is emerging as a "Green Solvent" in comparison to conventional extractants due to its unique properties like high decomposition temperature, low flammability and low volatility besides, its adjustable miscibility and polarity [Regel-Rosocka et al., 2011]. Potential of IL to extract rare earth metals from different medium was investigated by many researchers. Yang et al. [2013] have investigated the selective extraction and recovery of REMs from phosphor powders using IL 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ($[C_4mim][Tf_2N]$) with N, N-dioctyldiglycol amic acid (DODGAA) as the extractant. In

view of this, the present work has been carried out with the aim of synthesizing an ionic liquid based on two commercial extractants viz., Cyanex 272 (Acidic) and TEHA (Basic) and using it in the solvent extraction to separate and recover the rare earth metals particularly La(III) and Nd(III) separation.

2. Experimental

Stock solutions 10^{-2} M of La(III) and Nd(III) were prepared by dissolving their respective oxides in concentrated hydrochloric acid and diluting them to 100 cm^3 with distilled water. Initial metal ion concentration was maintained at 10^{-4} M for all extraction studies. Solvent extraction of La(III) and Nd(III) was investigated using tri-2-ethylhexyl ammonium bis(2,4,4-trimethylpentyl) phosphinate [$R_3N^+.Cy272^-$] as an extractant. The extraction reagent [$R_3N^+.Cy272^-$] was synthesized in the laboratory and purity of the reagent was checked by IR, NMR, Mass Spectra and elemental analysis. Solvent extraction experiments were conducted at room temperature by equilibrating equal volumes of aqueous solution containing desired metal ion concentration and the organic phase with the help of rotospin shaker for 45 min. Metal concentration in the raffinate was analyzed by ICP-OES and metal concentration in the organic phase was calculated by difference in the metal analysis of aqueous feed and that of raffinate.

3. Results and discussion

3.1. Effect of equilibrium pH on the extraction of La(III) and Nd(III)

Solvent extraction of La(III) and Nd(III) with 0.01M [$R_3N^+.Cy272^-$] was carried out at different equilibrium pH (1-5). Extraction of both the metals increased with the increase in equilibrium pH (Fig.1). It is also clear from the figure that Nd(III) is extracted at lower pH than La(III). The $pH_{0.5}$ values of Nd(III) and La(III) were found to be 3.7 and 4.5, respectively. The difference in $pH_{0.5}$ value (0.8) indicates the possibility of separation of La(III) and Nd(III). The difference in $pH_{0.5}$ values obtained using a commercial ionic liquid Cyphos IL-104 (Trihexyl (tetradecyl) phosphonium bis 2,4,4-trimethylpentylphosphinate) is found to be 0.7 where $pH_{0.5}$ values of La and Nd are 3.9 and 3.2 respectively. Table 1 shows the separation factor ($\beta = D_{Nd(III)} / D_{La(III)}$)

between Nd(III) and La(III) at different equilibrium pH using [R_3N^+.Cy272$^-$] as extractant. The separation factor values show increasing trend with increase in the pH of the solution after equilibration; $\beta_{Nd(III)/La(III)}$ is found to be low (12.25) at the lower equilibrium pH of 3.0. The best separation factor of 49 was obtained for Nd(III) vs. La(III) at the equilibrium pH= 4.5 and ionic liquid concentration of 0.01M.

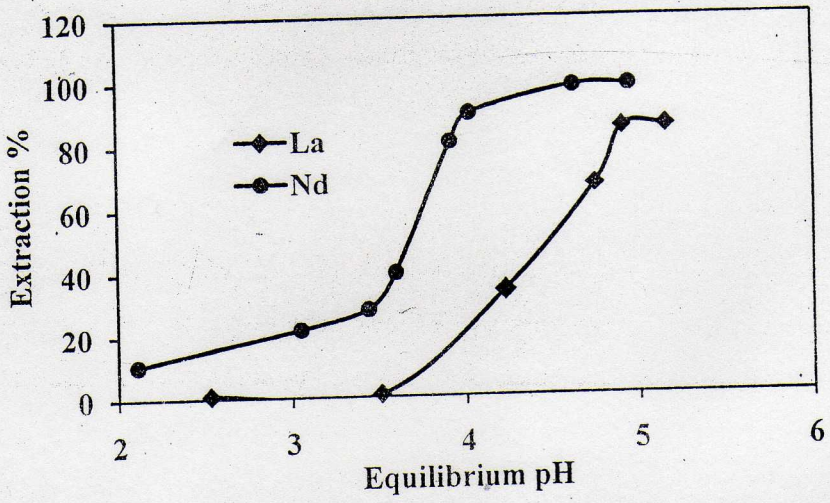


Fig.1. Effect of equilibrium pH on percentage extraction of Nd(III) and La(III).
[La^{3+}] or [Nd^{3+}] = 10^{-4}M, [R_3N^+][Cy272$^-$]= 0.01M, [Cl^-]= 0.1M.

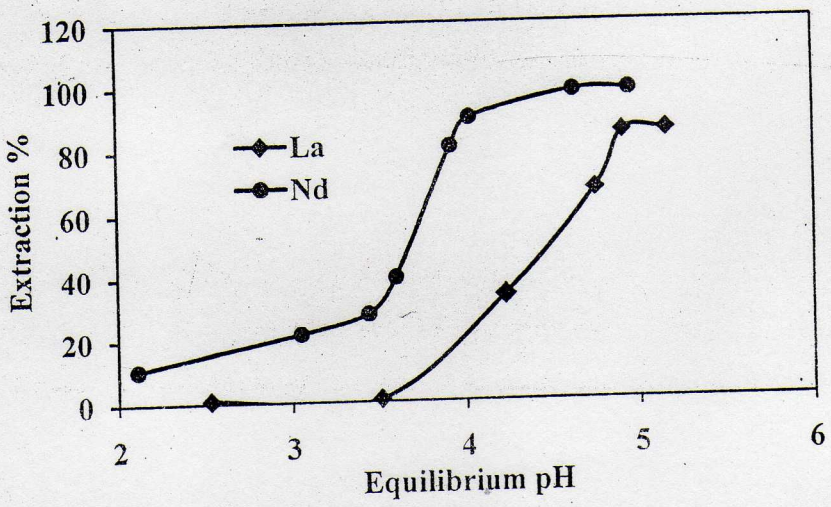
Table 1. Effect of equilibrium pH on the separation factor (S.F.) of Nd(III) and La(III).
[La^{3+}] or [Nd^{3+}] = 10^{-4}M, [R_3N^+][Cy272$^-$]= 0.01M, [Cl^-] = 0.1M

Eq. pH	3.0	3.5	3.7	4.0	4.2	4.5
S.F ($\beta_{Nd/La}$)	12.25	13.86	11.50	32.36	26.83	49.0

3.2. Effect of concentration of Ionic liquid on the extraction of LREEs [La(III) and Nd(III)]

Effect of concentration of ionic liquid ([R_3N^+][Cy272$^-$]) in the concentration range 0.001-0.01M was also investigated at a constant equilibrium pH of 4.0 (Fig. 2). The distribution co-efficient of both the rare earth metals increased with increase in ionic liquid concentration. The linear

between Nd(III) and La(III) at different equilibrium pH using [R_3N^+.Cy272$^-$] as extractant. The separation factor values show increasing trend with increase in the pH of the solution after equilibration; $\beta_{Nd(III)/La(III)}$ is found to be low (12.25) at the lower equilibrium pH of 3.0. The best separation factor of 49 was obtained for Nd(III) vs. La(III) at the equilibrium pH= 4.5 and ionic liquid concentration of 0.01M.



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Acknowledgments

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